SEM-EDS Analysis of Glass Fibers Corroded in Physiological Solutions by Dynamic Tests with Variable Flow Rates

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The dissolution of mineral fibers has been studied in simulated physiological fluids using a dynamic testing procedure. Fibers of different chemical composition and obtained by different processes with a mean diameter of about 1 μm, have been characterized with respect to their solubility under various test conditions of flow-rate. The surfaces were analyzed using scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and X-ray diffraction techniques. SEM examinations show the formation of various corrosion patterns: porous, gel-like outer layers; precipitation zones and even, in some cases, no modification of the surface aspect. EDS analyses performed on the fibers, on the fiber surface layers, or on the deposits show three types of chemical composition: areas enriched in Al, in Ca and P, or in Al, Ca, and P. These surface compositions can be found for the same type of fiber tested, depending on the flow rate of the solution. Surface changes depend strongly on the initial composition of the glass and on the test conditions, particularly the flow rate. It is of particular interest to characterize the remaining surfaces (if any) obtained at the end of the *in vitro* test run and to compare them with surface analysis of the recovered fibers from the *in vivo* tests to assess the validity of the *in vitro* tests. — Environ Health Perspect 102(Suppl 5):73–75 (1994)

Key words: vitreous fiber, durability, *in vitro* assessment, glass leaching, physiological attack, scanning electron microscopy, energy dispersive spectrometry

Introduction

The study of corroded glass fibers recovered from the lungs of test animals after an in vivo inhalation test is complicated and very expensive. It is much easier to simulate the phenomena by immersing the fibers for variable times in a solution whose composition is close to that of the physiological environment. Several solutions have been proposed (*1,2*). However, the experimental conditions of the test, irrespective of the composition of the solution, must be as close as possible to the natural conditions. Parameters that may play an important role include the quantity of tested fibers, the dispersion of the fibers in the solution, and the flow rate of the solution around the fibers (*3*). In this study, solution flow rates have been varied.

Experimental Methods

Different glass fibers, whose compositions are given in Table 1, have been investigated. The samples C3, CM25, CM38, and CM44 were obtained by the TOR process, with a mean diameter of about 1 μm. MMVF 10, 11, 21, and 22 were prepared by Manville from industrial glass fibers; they also have a mean diameter of about 1 μm (MMVF 11 is a C3 type composition). Experimental conditions of the corrosion tests have been described by Scholze and Conradt (*4*) and are summarized as follows: mass of glass = 0.2 g; flow rate of the solution = 40, 300, and 1600 ml/day; solution buffered at pH 7.6; and test times of 42 days (28 days for some samples).

After reaction, the fibers were removed from the filter, rinsed in pure water and in ethanol, and then dried. The fluid collected was chemically analyzed, and the quantity of silica was used to evaluate the corrosion rate. We focused on the modifications of the surface of the fibers in terms of both morphology and chemical composition.

The morphology of the fibers has been characterized by scanning electron microscopy (SEM) after the samples have been covered by a conducting layer (generally carbon, but sometimes gold, when the only interest is in obtaining morphological information).

The composition of the surface of the fibers was evaluated by energy dispersive spectroscopy (EDS). The technique is suit-

Table 1. Composition (wt-%) of the glasses used in this study.

	C3	CM25	CM38	CM44	MMVF10	MMVF11	MMVF21	MMVF22
SiO_2	65.0	65.0	62.0	61.3	57.5	63.4	46.2	38.4
SO_3	0.25	0.17	0.20	0.04	0.12	0.33	0.23	1.81
Fe_2O_3	0.17	0.06	0.06	0.08	0.07	0.25	7.0	0.3
Al_2O_3	3.4	2.0	0.15	1.0	5.1	3.9	13.0	10.6
CaO	7.0	7.8	16.0	6.7	7.5	7.5	16.9	37.5
MgO	3.0	3.3	3.0	2.7	4.1	2.8	9.3	9.9
Na_2O	15.8	15.8	15.2	15.5	15.0	15.5	2.6	0.4
K_2O	0.7	0.4	0.1	0.7	1.1	1.3	1.3	0.5
B_2O_3	4.5	4.3	3.2	11.0	8.8	4.5		
TiO_2	0.2	0.1					3.0	0.5
P_2O_5		1.2		1.0			0.2	
F					0.8			

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Table 2. Energy dispersive spectrometry (EDS) analysis of fibers in wt-%.

	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	P_2O_5	Cl	Fe_2O_3	TiO_2
Accuracy, %	15	15	20	10	30	30	10	15	30	30	30
C3 unlixivied	17.2	3.5	3.7	65.6	<0.2	1.2	8.4	<0.2	<0.2		
" lixivied 40 ml/day	14.9	3.1	6.6	68.5	<0.2	0.8	5.6	0.3	0.2		
" lixivied 1600 ml/day	11.7	3.1	5.6	53.4	1.0	0.7	14.8	9.3	0.5		
CM25 unlixivied	18.0	3.2	2.8	66.7	<0.2	0.7	7.9	0.6	0.2		
" lixivied 40 ml/day	9.0	1.3	10.0	74.3	0.5	0.4	2.4	0.7	1.4		
" lixivied 1600 ml/day	8.5	3.5	5.5	41.9	0.8	0.6	22.7	16.0	0.6		
CM38 unlixivied	18.4	3.4	0.4	61.4	<0.2	0.7	15.0	0.6	<0.2		
" lixivied 40 ml/day	2.5	1.3	1.4	22.4	0.7	0.2	41.0	30.4	0.2		
" lixivied 1600 ml/day	3.3	4.9	0.3	1.6	0.2	0.2	50.8	37.2	1.6		
CM44 unlixivied	20.5	2.9	1.4	65.1	1.0	0.6	7.1	1.2	<0.1		
" lixivied 40 ml/day	8.3	2.2	1.3	72.0	0.5	0.2	9.8	5.6	0.2		
" lixivied 300 ml/day	5.0	2.4	2.9	64.0	0.4	0.2	14.1	10.6	0.2		
" lixivied 1600 ml/day	4.9	4.7	2.5	13.7	0.5	0.1	40.5	31.4	1.7		
MMVF10 unlixivied	16.1	4.9	5.0	62.0	<0.2	1.5	10.3	0.3	<0.2	<0.2	
" lixivied 40 ml/day	16.3	0.9	12.8	66.2	0.2	0.3	0.8	0.5	2.0	<0.2	
" lixivied 300 ml/day	8.8	2.2	10.9	72.7	<0.2	0.2	4.5	0.3	0.2	0.2	
" lixivied 1600 ml/day	1.8	2.6	12.7	48.5	0.2	0.1	21.8	11.9	0.2	0.2	
MMVF11 unlixivied	16.6	2.9	3.2	66.8	<0.2	1.6	8.7	<0.2	<0.2	<0.2	
" lixivied 40 ml/day	17.7	2.5	7.1	63.9	0.3	0.9	4.3	0.9	2.4	<0.2	
" lixivied 300 ml/day	13.9	2.8	6.3	68.9	0.2	0.9	6.3	0.2	0.2	0.2	
" lixivied 1600 ml/day	4.8	2.6	8.5	59.9	0.2	0.3	14.0	8.9	0.2	0.5	
MMVF21 unlixivied	4.5	10.0	13.5	42.2	<0.2	1.4	15.2	0.5	<0.2	10.1	2.5
" lixivied 40 ml/day	6.2	9.0	12.5	42.1	0.3	1.0	15.7	0.7	0.2	9.5	2.9
" lixivied 300 ml/day	3.4	9.6	13.4	43.9	<0.2	1.1	16.0	0.3	<0.2	9.4	2.8
" lixivied 1600 ml/day	3.5	9.4	13.2	42.3	<0.2	1.2	16.4	0.6	<0.2	10.4	2.9
MMVF22 unlixivied	1.0	8.2	8.0	36.7	1.4	0.5	44.1	<0.2	<0.2	<0.2	<0.2
" lixivied 40 ml/day	2.4	7.6	11.3	40.0	0.9	0.4	32.2	4.0	<0.2	1.2	<0.2
" lixivied 300 ml/day	1.9	8.5	12.3	43.0	1.2	0.3	30.6	1.7	<0.2	<0.2	0.5
" lixivied 1600 ml/day	1.8	5.9	14.8	52.2	0.6	0.4	21.2	1.5	<0.2	1.0	0.7

able for this problem, first, because localized analyses are possible, which is very important, considering the size of the fibers and of the deposits. Second, although the thickness analyzed (about 1 μm) is large, it is acceptable if the thickness of the corroded layer is in the scale of 0.1 to 1 μm. However, the composition obtained is often an average between the deposits (or the corroded layer) and the underlying glass.

The technique has some disadvantages, however, the most important being the impossibility of detecting boron in glass. Boron is a major constituent of most glass fibers and may play a key role in the corrosion mechanism. Due to the shape of the samples, which makes curvature radius a key parameter, the reproducibility is poor (10–20% for major elements), but by repeating the analyses, which takes less than 2 min each, the lack of reproducibility can be overcome.

After every corrosion test, a set of three samples was taken to improve the reliability, since the mass analyzed from ten points is only about 2.5×10^{-11} g, which is very low compared to the sample of 0.2 g.

Results

Morphological Aspects

Whereas untested fibers are always perfectly smooth, with the exception of some dusts, corroded fibers often have a perturbed surface which may present several morphologies. For example, there may be a relatively uniform layer, with many cracks (for instance C3, CM25, MMVF 10 and 11 at low flow rate) (Figure *1A*). Alternatively, there may be many deposits (thickness of about 0.2 μm) either star-shaped or completely covering the surface of the fibers (for instance, C3, CM25, MMVF 10 and 11 at high flow rate (Figure *1B*), CM38 and CM44 regardless of flow rate). The last alternative could be that the surface, as was the case with MMVF 21, remained almost unchanged regardless of the flow rate.

Analytical Aspect

In parallel with the different morphological aspects of the corroded glass fibers, different surface compositions have been observed. Table 2 presents these as the mean of five to ten points on each sample.

The morphological form (form 1) is characterized by a decrease of every element except Si and Al, which may increase, by 100%.

In form 2, deposits are always highly enriched in Ca and P, with the ratio P_2O_5/CaO close to that calculated for apatite. The concentration of P_2O_5 versus CaO has been plotted for every point of CM25 corroded fibers (Figure 2). A similar curve was obtained for the other fibers presenting deposits.

In form 3, MMVF 21 fibers, which seem uncorroded from the SEM images, always have the same composition as the untested fibers. This means that the dissolution is congruent or very low.

Very often forms 1 and 2 may be observed at the same time with a relatively uniform layer enriched in Al and deposits containing Ca and P.

Discussion

There seem to be three main corrosion mechanisms for the glass fibers investigated. The first is the formation of a silica gel layer containing a high concentration of Al_2O_3, and probably some Na_2O. This cor-

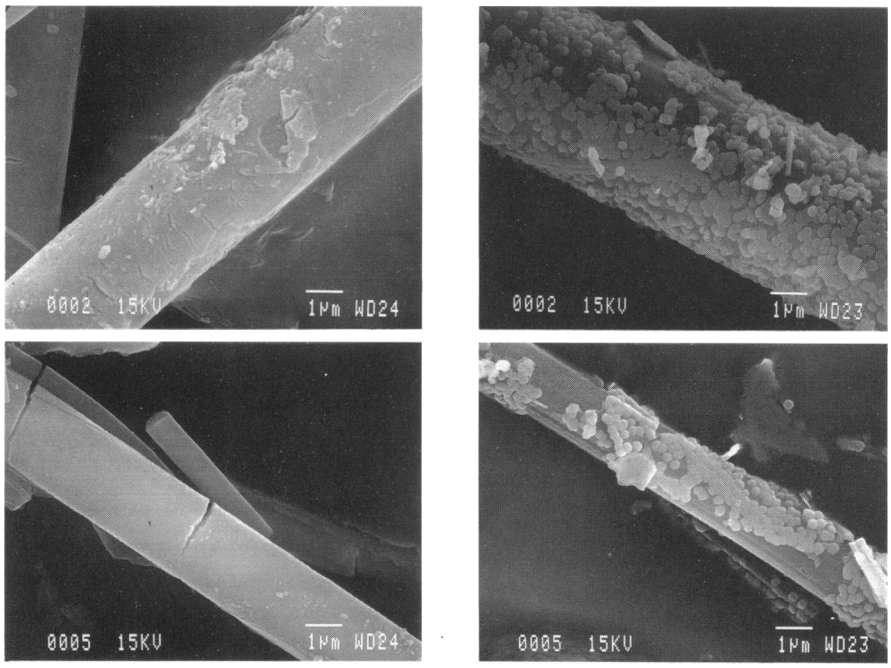

Figure 1. *A*, SEM secondary electron images of fibers CM25 lixivied at 40 ml/day. *B*, Lixivied at 1600 ml/day).

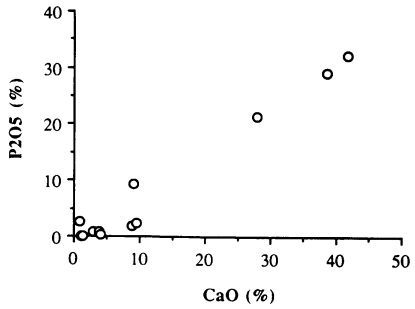

Figure 2. Variation of P_2O_5 versus CaO from EDS analysis of CM25 lixivied fibers (in wt-%).

rosion is classic for soda-lime glass corroded in water (*5,6*). The concentration of Al_2O_3 reaches a level of about 15 to 20% in weight, so that, as the corrosion progresses, the thickness of this layer increases. The silica gel layer is always reorganizing itself as the corrosion progresses. The second corrosion mechanism is the formation of deposits containing CaO and P_2O_5 with a composition close to apatite, although X-ray diffraction patterns performed on fibers with large amounts of Ca-P deposits are characteristic of noncrystalline solids. The third mechanism is a congruent dissolution. In this case, one cannot see any change in the surface composition compared with the initial composition. It is impossible, from the point of view of the surface composition, to distinguish a congruent dissolution from the absence of corrosion. MMVF 21 fibers are an example; but in this case, analyses of Si in the solution do show that Si dissolution takes place at a low rate and of the same order of magnitude as with MMVF 22, where there is a modification of the surface composition. It must be assumed that MMVF 21 fibers present a congruent dissolution, within the limits of the analytical technique.

Very often the first two mechanisms are visible at the same time on the same sample. The factors determining this type of corrosion mechanism are not clear. A high corrosion rate, however, is often associated with the formation of Ca-P deposits, as with CM 25 fibers, where these deposits are observed only at high flow rate, corresponding to a higher corrosion rate (Table 2). Similarly, compositions with high level of CaO or P_2O_5, which often correspond to a high corrosion rate, easily lead to the formation of Ca-P deposits. The presence of P_2O_5 in the glass composition, however, is not necessary to form such deposits. C3 fibers, for instance, which have no P_2O_5, form Ca-P deposits at a high flow rate.

It is difficult to understand why increasing the flow rate results in Ca-P deposits. Increasing the flow rate increases the corrosion rate, but also decreases the concentration of Ca and P in the solution, to the extent that there are Ca and P in the fibers. The solubility product of apatite is not reached more easily at a high flow rate, so there must be other factors to explain this phenomenon. It is possible that there is a boundary layer that is not affected by flow rate variations; or, alternatively, flow rate variations may affect the rate of nucleation.

Conclusion

We have shown that the flow rate during *in vitro* corrosion tests of glass fibers greatly influences not only the corrosion rate, which increases with increased flow rate, but also, very often, the corrosion mechanism. For instance, C3, CM 25, MMVF 10 and 11 fibers show a relatively uniform surface layer, mainly rich in SiO_2 and Al_2O_3 at a low flow rate, but the same fibers form fine Ca-P deposits on their surface at a high flow rate. However, more soluble glasses (CM 38 and CM 44) always lead to the formation of such deposits, regardless of the flow rate (ranging from 40 ml/day to 1600 ml/day). There are no Ca-P deposits on fibers of low silica solubility (MMVF 21 and 22), whatever the flow rate.

These results show the importance of knowing the corrosion mechanism of fibers found in *in vivo* tests so that we can adjust the experimental conditions to achieve a comparable mechanism in the *in vitro* tests.

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